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COMPLIANCE MONITORING OF PURGEABLE ORGANICS WITH MASS SPECTROMETRY

by

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16. ABSTRACT

During the past two years two new Methods have been approved for nationwide use for detection and measurement of the four regulated trihalomethanes (THMs) in drinking water.[1] This increases to four the number of available methods for compliance monitoring of THMs. Two of those methods (numbers 501.1 and 501.2) were published in the Federal Register in 1979[2] and are, therefore, well known to drinking water analysts. The purpose of this paper is to discuss monitoring with the two new methods (numbers 501.3 and 524)[3,4] and the advantages and disadvantages of each.

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Compliance Monitoring of Purgeable Organics with Mass Spectrometry

INTRODUCTION

During the past two years two new methods have been approved for nationwide use for detection and measurement of the four regulated trihalomethanes (THMs) in drinking water.[1] This increases to four the number of available methods for compliance monitoring of THMs. Two of those methods (numbers 501.1 and 501.2) were published in the Federal Register in 1979[2] and are, therefore, well known to drinking water analysts. The purpose of this paper is to discuss monitoring with the two new methods (numbers 501.3 and 524) [3,4] and the advantages and disadvantages of each.

APPROVED METHODS FOR COMPLIANCE MONITORING

Because a discussion of approved methods for compliance monitoring (Table 1) requires continual differentiation among these four methods, using the method number permits easy reference to a particular method. The first digit in these method numbers indicates the type of sample matrix; drinking water methods are 500 series methods. The second and third digits indicate the particular analytes to which the method is applicable - the three 501 methods were designed specifically for THMs. The digit following the decimal indicates differences in extraction procedure, sample size or detector. Method 524[4] is a general-purpose drinking water method that includes THMs among many other analytes. It received the 524 number because

of its similarities to Method 624[5], one of the 600-series methods for industrial effluents and wastewaters.

All four drinking water methods require removal of the analytes from the drinking water sample, separation of the analytes from one another, and detection and measurement of each analyte. In Method 501.2, analytes are removed from a 10-mL drinking water sample by extraction with 2 mL of a solvent. The other three use purge-and-trap procedures in which sufficiently volatile organic compounds are removed when an inert gas such as helium is bubbled through the water. The helium and purged compounds enter a trap containing sorbent materials that permit the helium to pass but retain the purged organic compounds. These methods all involve separation of analytes with a gas chromatograph (GC). Methods 501.1 and 501.2 use halide specific or electron capture GC detectors; Methods 501.3 and 524 use a mass spectrometer (MS) as a GC detector.

THE MS AS A GC DETECTOR

The basic advantage of the MS as a GC detector is that it provides composition information about a sample component eluting from the GC. A block diagram (Figure 1) illustrates the basic features of a GC/MS system, which almost always includes a dedicated computer, commonly called the data system (DS).

Upon entering the MS, analyte molecules encounter a stream of electrons emitted from a hot filament. Bombarding electrons cause analyte molecules to lose electrons and atoms and form positive ions. If only one electron is lost, the ion that is formed has a mass essentially the same as the original

molecule, and that ion is called a molecular ion. If the molecule loses an atom or groups of atoms, fragment ions are formed. Most frequently electron bombardment procedures a combination of molecular and fragment ions.

Ions are subjected to conditions that cause them to travel through the mass analyzer at different rates, depending on the mass to charge ratio (m/z). Detecting and recording the m/z as a function of the time produces a mass spectrum, whose features depend on the composition and structure of the compound producing it.

Because the GC eluent continually enters the MS, the molecules being fragmented continually change. Therefore, rapid and frequent detection of ions and their relative abundances is necessary. Hence, the need for a computer to control the MS and to receive and store the data. The range of masses to be detected depends on molecular weights of analytes of interest. With purgeable compounds, this range is usually about 40 to 250 atomic mass units. The computer is programmed to control MS operation to permit repetitive acquisition of mass spectra; a spectrum may be acquired every second. Each spectrum is stored with a reference number called a spectrum number and all spectra acquired for a particular sample comprise a data file. After all sample components have eluted from the GC, the stored spectra in the data file can be retrieved and displayed.

A display of the sum of all ions in each spectrum plotted versus spectrum number produces a total ion current profile (TICP, Figure 2), which is equivalent to a gas chromatogram. The analyst then may display a sample component mass spectrum by selecting a particular spectrum number and plotting masses versus relative intensity.

The data system software permits manipulation of MS data to enhance a spectrum when the GC does not completely separate sample components or to eliminate contributions from column packing materials and background ions. Using the TICP, the analyst selects an appropriate background spectrum and instructs the computer to subtract it from the spectrum of the sample component of interest.

MONITORING THMS WITH METHOD 501.3

Although the MS has the great advantage of providing structural information about sample components, it is not as sensitive as some other GC detectors. To detect and measure low levels of THMs in a 5-mL drinking water sample, the sample size used with conventional GC detectors, a special MS technique is required. Instead of acquiring information about all the ions produced by a sample component, only a few ions that are characteristic of an analyte of interest are detected and measured. Sensitivity is increased because available data acquisition time is spent on only a few ions rather than about 200 ions. The few ions to be detected and measured must be carefully selected; hence the name, selected ion monitoring (SIM). The monitored ions must be relatively abundant (therefore producing intense signals), and be relatively unique (i.e., must not be present as a background ion and must not be produced by other organic compounds that have the same GC retention characteristics as analytes of interest). For the THMs, monitored ions are the two most abundant ions in the mass spectrum (Figure 3) of each compound. Examination of mass spectra of chloroform and bromodichloromethane shows that the two most intense ions are m/z 83 and 85 for both compounds. These ions are identical and are produced by the loss

of chlorine and bromine, respectively, from chloroform and bromodichloromethane. Because these two compounds have significantly different GC retention times, the same two ions can be used to detect and measure both compounds. The other two THMs, bromoform and chlorodibromomethane, produce major fragments with isotopic clusters around m/z 171, 173 and 175 and 127, 129 and 131, respectively (Figure 4). The two most abundant ions in each cluster are used to monitor each of these compounds. One ion must be monitored to detect and measure fluorobenzene, the internal standard. Therefore, the capability to monitor a total of seven ions is required to measure the THMs and the internal standard (Table 2).

After data acquisition, display of data for all seven ions monitored produces a selected ion current profile showing all five compounds (Figure 5). Although some other purgeable organohalides have the same retention times as THMs with the recommended GC columns, these compounds are not observed because they do not produce the ions selected for monitoring. A representative chromatogram of halogenated organic compounds (Figure 6) shows no components coeluting with chloroform or bromodichloromethane. Chlorodibromomethane, however, coelutes with 1,1,2-trichloroethane and cis-1,3-dichloropropene. Because neither of the latter two compounds produces ions at m/z 127 or 129 (which are the ions used to detect and measure chlorodibromomethane), they will not interfere with measurement of chlorodibromomethane. A similar situation exists with the coelution of bromoform (monitored with m/z 171 and 173) and 1,1,1,2-tetrachloroethane, which produces neither m/z 171 or 173.

Nonhalogenated compounds will not be falsely identified as THMs. Two

ions are monitored to detect isotopic clusters that are produced by THMs but not by nonhalogenated compounds. Those two ions must maximize simultaneously and have the appropriate relative intensities. In addition, the monitored ions must be detected at the same retention time observed for the appropriate THM standard. Therefore, with Method 501.3 the THMs can be identified and measured with data acquired for only seven ions.

MONITORING THMs WITH METHOD 524

The mass spectroscopist, however, abhors the thought of not taking advantage of the full capabilities of the GC/MS/DS. With little extra effort and the same equipment and time, information can be obtained about many sample components in addition to THMs. That is the major advantage of Method 524 over other approved THM methods. For Method 524, the sample size was increased from 5 mL to 25 mL and full-range mass spectra were acquired to demonstrate acceptable sensitivity, accuracy and precision for THMs (Table 4). Although the method detection limit (MDL)[6] is higher with Method 524 than with Method 501.3, the sensitivity with the former is quite acceptable for THM compliance monitoring. The single laboratory data indicate that accuracy is better with 524 than with 501.3, but the relative standard deviation of seven measurements was consistently better with 501.3.

MONITORING OTHER ANALYTES WITH METHOD 524

In addition to THMs, Method 524 has been tested with 24 other purgeable compounds that are potential drinking water contaminants. Data acquired in

the single laboratory study indicated that Method 524 can be used to identify and measure many sample components in addition to THMs (Table 5). If particular purgeable compounds are known to be a problem either continually or intermittently in a particular area, with Method 524 those compounds can be monitored along with THMs. For example, a water treatment plant operator may know that benzene and toluene are frequently present in the plant's source water and should be monitored along with THMs in the finished water. Neither benzene nor toluene would be detected with the other three THM methods; the appropriate ions are not monitored with the other MS method, and the GC detectors used for 501.1 and 501.2 will not detect non-halogenated compounds.

With Method 524, as with other methods, known amounts of a standard of each analyte of interest must be analyzed to determine its GC retention time, to measure its mass spectrum, and to determine how the detector responds to varying amounts of that compound. After acquisition of sample component data, the analyst can examine the total ion current profile and determine if any detected sample component has the appropriate retention time for any analyte of interest. By retrieving the appropriate sample component spectrum and comparing it to the standard spectrum previously acquired, the analyst can determine if the sample component is the compound of concern. If so, its concentration can be measured with the concentration calibration data already acquired.

A major advantage of Method 524 is that it permits identification of unexpected contaminants. The analyst selects sample component spectra and compares each to mass spectra in a data base. Because current collections

of mass spectra contain about 40,000 different compounds, that could be a laborious and time consuming task. The computer, however, can perform that task quickly and without tiring or making careless mistakes. The result is a list of compounds whose spectra best match that of the unknown sample component. The analyst must, however, examine the matches and judge the validity.

The minimum amount of compounds other than THMs that can be detected with Method 524 is variable; MDLs are compound dependent, varying with purging efficiency and concentration (Table 5). MDL is defined[6] as the calculated minimum amount that can be measured with 99% confidence that the reported value is greater than zero. For the tested analytes in reagent water, MDLs vary from 0.07 to 11.2 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations.

POTENTIAL REGULATED COMPOUNDS

In an Advanced Notice of Proposed Rule Making (ANPRM)[7] issued March 4, 1982, EPA listed 12 specific compounds and two groups of volatile organic compounds that are being considered for regulation (Table 6). Most of those are included among compounds tested with Method 524. Those not included are cis-1,2-dichloroethylene, 1,4-dichlorobenzene, and trichlorobenzenes. Trichlorobenzenes do not elute from the column that was used to collect these Method 524 data. Other columns, however, are quite acceptable, and the column can be selected to fit the special needs of a particular place

and time. Trichlorobenzenes have been shown[8] to be sufficiently purgeable, and no reason exists for their being incompatible with Method 524. Based on data obtained for similar compounds, 1,1-dichloroethylene and trans-1,2-dichloroethylene (Table 6), that were tested with Method 524, one would predict that cis-1,2-dichloroethylene would not be detected at low microgram per liter concentrations but could be detected and measured with reasonable accuracy at concentrations greater than 20 µg/L. One of the two dichlorobenzenes tested performed well at a concentration of 1.6 µg/L; the other, not so well. Both, however, presented no problems at a concentration of 16 µg/L.

In the ANPRM, potential maximum contaminant levels were presented for only six compounds (Table 6). For five compounds, the potential MCL was a range: 5 to 500 µg/L for three compounds (trichloroethylene, tetrachloroethylene and carbon tetrachloride) and 1 to 100 µg/L for two compounds (1,2-dichloroethane and vinyl chloride). The potential MCL for the remaining listed compound, 1,1,1-trichloroethane, was 1000 µg/L. With those MCLs, vinyl chloride is the only listed compound that is a potential problem if Method 524 is used for drinking water analysis. That potential problem exists only at the lower concentration end of the stated potential MCL range. The mean method efficiency for vinyl chloride was only 54%, and its MDL was calculated to be 8.5 µg/L. If, however, concentrations above about 20 µg/L are of concern, Method 524 should provide acceptable results for vinyl chloride.

CONCLUSIONS

Compliance monitoring with mass spectrometry can be efficient and cost effective, because this technique permits detection and measurement of many purgeable compounds in addition to THMs. The cost of GC/MS systems has frequently been cited as a concern to laboratory managers. Instrument manufacturers now offer a wide range of GC/MS systems. A recent innovation incorporates a personal computer; the price of the total system is approximately $30,000, which is comparable to prices of contemporary automated GCs with multiple detectors. The mystique formerly associated with the mass spectrometer as a gas chromatographic detector should no longer be a concern either; an effective operator does not have to be a trained mass spectroscopist.

REFERENCES

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2. "Appendix C. Analysis of Trihalomethanes in Drinking Water," Fed. Reg., Vol. 44, No. 231, p. 68672-68690 (November 29, 1979).

3. "Method 501.3. Measurement of Trihalomethanes in Drinking Water with Gas Chromatography/Mass Spectrometry and Selected Ion Monitoring," Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, March 1982.

4. "Method 524. Measurement of Purgeable Organic Compounds in Drinking Water by Gas Chromatography/Mass Spectrometry," Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, February 1983.

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7. "National Revised Primary Drinking Water Regulations, Volatile Synthetic Organic Chemicals in Drinking Water," Fed. Reg., Vol. 47, No. 43, p. 9350-9358, March 4, 1982.

8. "Method 503.1. The Analysis of Aromatic Chemicals in Water by the Purge and Trap Method, Environmental Monitoring and Support Laboratory, U.S. Environmental Protection Agency, Cincinnati, Ohio, EPA-600/4-81-057, May 1980.

Table 1. Approved Methods for THM Compliance Monitoring

Method No.	Date	Analytes	Tech.	Ext. Tech.	Sep. Detector	Sample Size
501.1	1979	THMs	Purge/Trap	GC	Halogen Specific	5 mL
501.2	1979	THMs	Liquid/Liquid	GC	EC	10 mL
501.3	1982	THMs	Purge/Trap	GC	MS	5 mL
524	1983	Purge-ables	Purge/Trap	GC	MS	25 mL

Table 2. Ions Used to Monitor
Trihalomethanes and Internal Standard

Compound	Ion	m/z	Theoretical Rel. Abun., %
$CHCl_3$	$CHCl_2^+$	83	100
		85	65
$CHCl_2Br$	$CHCl_2^+$	83	100
		85	65
$CHClBr_2$	$CHClBr^+$	127	65
		129	100
$CHBr_3$	$CHBr_2^+$	171	51
		173	100
C_6H_5F	$C_6H_5F^+$	96	100

Table 3. Possible Interferences with Method 501.3 for Compliance Monitoring

Compound	Monitored Ions	Possible Coeluting[a] Halogenated Compound	Effect
$CHCl_3$	83, 85	None	None
$CHBrCl_2$	83, 85	None	None
$CHBr_2Cl$	127, 129	1,1,2-trichloroethane cis-1,3-dichloropropene benzene	None; m/z 127 or 129 not produced
$CHBr_3$	171, 173	1,1,1,2-tetrachloroethane	None; m/z 171 or 173 not produced

a Because both prescribed GC columns produce similar retention patterns, possible interferences are the same for both columns.

Table 4. Measurement[a] of THMs with MS Methods

Analyte	Method 524				Method 501.3			
	True Value µg/L	Accuracy %	RSD %	MDL[b] µg/L	True Value µg/L	Accuracy %	RSD %	MDL[b] µg/L
$CHCl_3$	1.6	100	3.8	0.20	0.2	97.5	9.7	0.06
	16	100	2.0		20	94.9	2.8	
$CHBrCl_2$	1.6	100	5.5	0.29	0.2	103.0	10.2	0.07
	16	98.8	3.2		20	93.7	3.6	
$CHBr_2Cl$	1.6	100	6.5	0.34	0.2	103.0	7.6	0.05
	16	93.8	13.6		20	90.8	5.8	
$CHBr_3$	1.6	93.8	6.5	0.34	0.2	106.0	5.8	0.04
	16	96.9	12.7		20	91.5	8.4	

a Mean values produced by single-laboratory analysis of seven aliquots of spiked reagent water.

b Method detection limit - calculated minimum concentration that can be measured with 99% confidence that reported value is greater than zero.

Table 5. Method 524 Data[a] for Analytes Other than THMs

Compound	MDL[b] µg/L	Accuracy[c] %	RSD %
chloromethane	9.2	103.1	16.6
vinyl chloride[d]	8.5	113.8	13.9
methylene chloride[d]	0.25	98.8	2.1
1,1-dichloroethylene[d]	0.27	101.9	10.8
trans-1,2-dichloroethylene[d]	1.7	96.3	14.5
1,2-dichloroethane[d]	0.35	100	10.5
1,1,1-trichloroethane[d]	0.13	101.3	4.9
carbon tetrachloride[d]	0.13	100	2.4
1,1,2-trichloroethane	1.0	99.4	15.9
trichloroethylene[d]	0.18	100	1.1
benzene	0.21	100.6	3.1
cis-1,3-dichloropropene	1.8	93.8	11.7
1,1,2,2-tetrachloroethane	0.28	96.9	11.5
tetrachloroethylene[d]	0.07	98.8	2.4
toluene	0.08	99.4	1.6
chlorobenzene[d]	0.09	98.1	3.6
1,2-dibromo-3-chloropropane	10.1	98.1	19.1
styrene	1.3	98.8	10.4
p-xylene	0.18	100.6	1.0
bis(2-chloroisopropyl)ether	8.6	94.4	15.1
1,3-dichlorobenzene[d]	1.3	95.0	9.8
1,2-dichlorobenzene[d]	0.3	98.1	8.3

a Data produced by analysis of seven aliquots of reagent water spiked with known amounts of each compound.

b MDLs calculated from measurement of 1.6 µg/L concentrations except for compounds that were inefficiently purged and were not detected in 1.6 µg/L solutions; then MDLs were calculated using 16 µg/L solutions.

c Accuracy of measurements of 16 µg/L concentrations.

d A chemical being considered for regulation.

Table 6. Chemicals Being Considered for Regulation

	Potential[a] MCL, µg/L	MDL[b] µg/L	Method 524 Method Efficiency,[c] %
Trichloroethylene	5 to 500	0.18	100; 107
Tetrachloroethylene	5 to 500	0.07	106; 108
Carbon tetrachloride	5 to 500	0.13	106; 110
1,1,1-trichloroethane	1000	0.13	94; 91
1,2-Dichloroethane	1 to 100	0.35	63; 56
Vinyl chloride	1 to 100	8.5	—; 54
Methylene chloride	—	0.25	119; 82
Benzene	—	0.21	106; 96
Chlorobenzene	—	0.09	94; 96
Dichlorobenzenes	—	0.3	81; 79
1,2-dichlorobenzene	—	1.3	75; 83
1,3-dichlorobenzene	—	?	?
1,4-dichlorobenzene	—	?	?
Trichlorobenzenes	—	0.27	94; 88
1,1-dichloroethylene	—	?	?
cis-1,2-dichloroethylene	—	1.7	50; 99
trans-1,2-dichloroethylene	—		

a MCL - Maximum Contaminant Level
b MDL - Method Detection Limit
c Mean Method Efficiency - first number determined with reagent water spiked with 1.6 µg/L; second number determined with reagent water spiked with 16 µg/L.

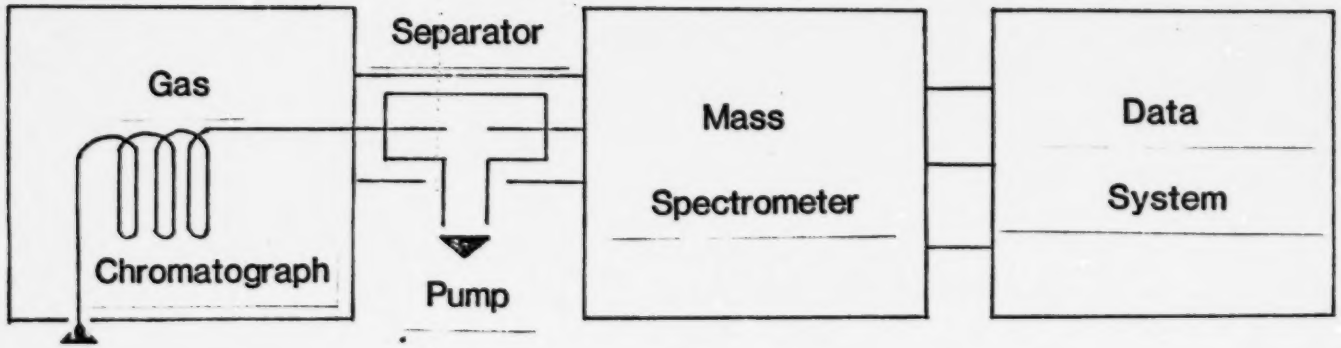

Figure 1. Block Diagram of a GC/MS/DS

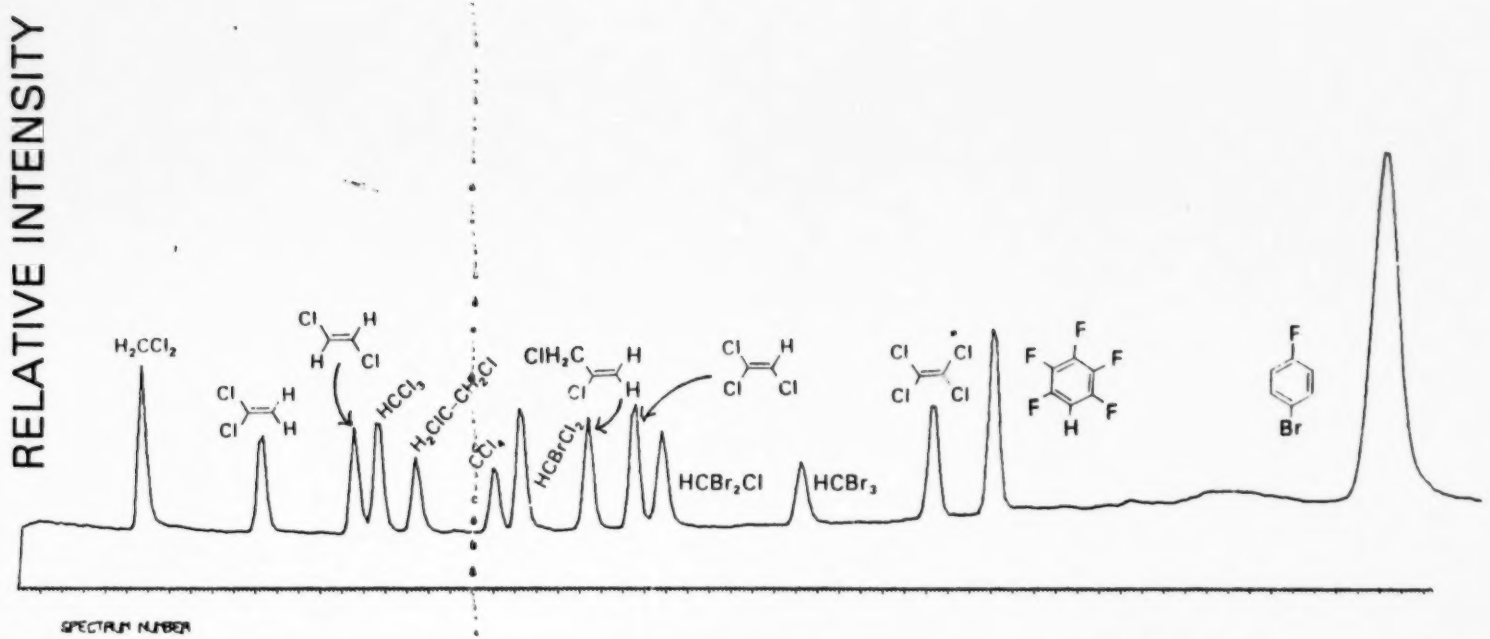

Figure 2. A Total Ion Current Profile

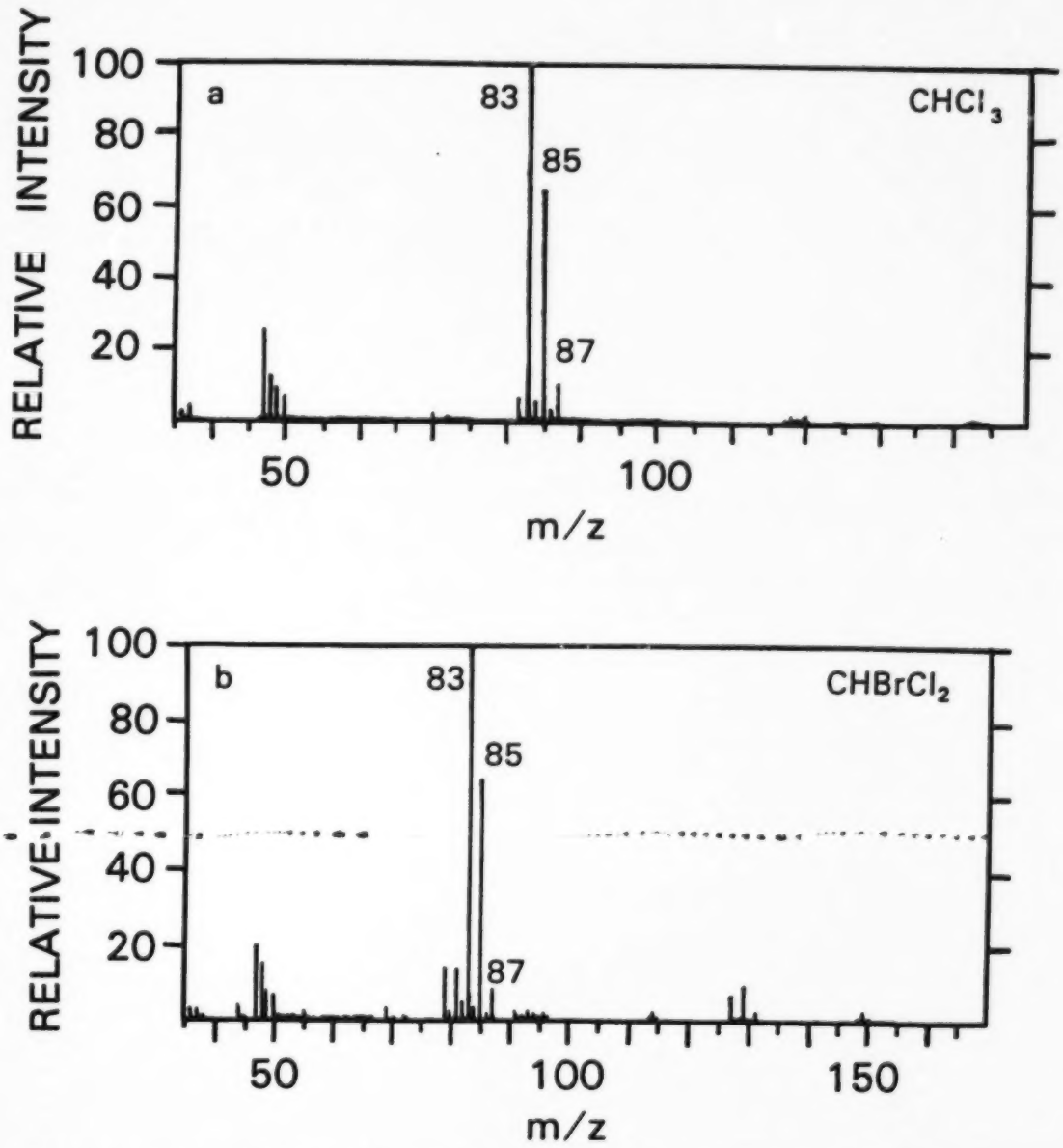

Figure 3. Mass Spectra Of Chloroform (a) And Bromodichloromethane (b)

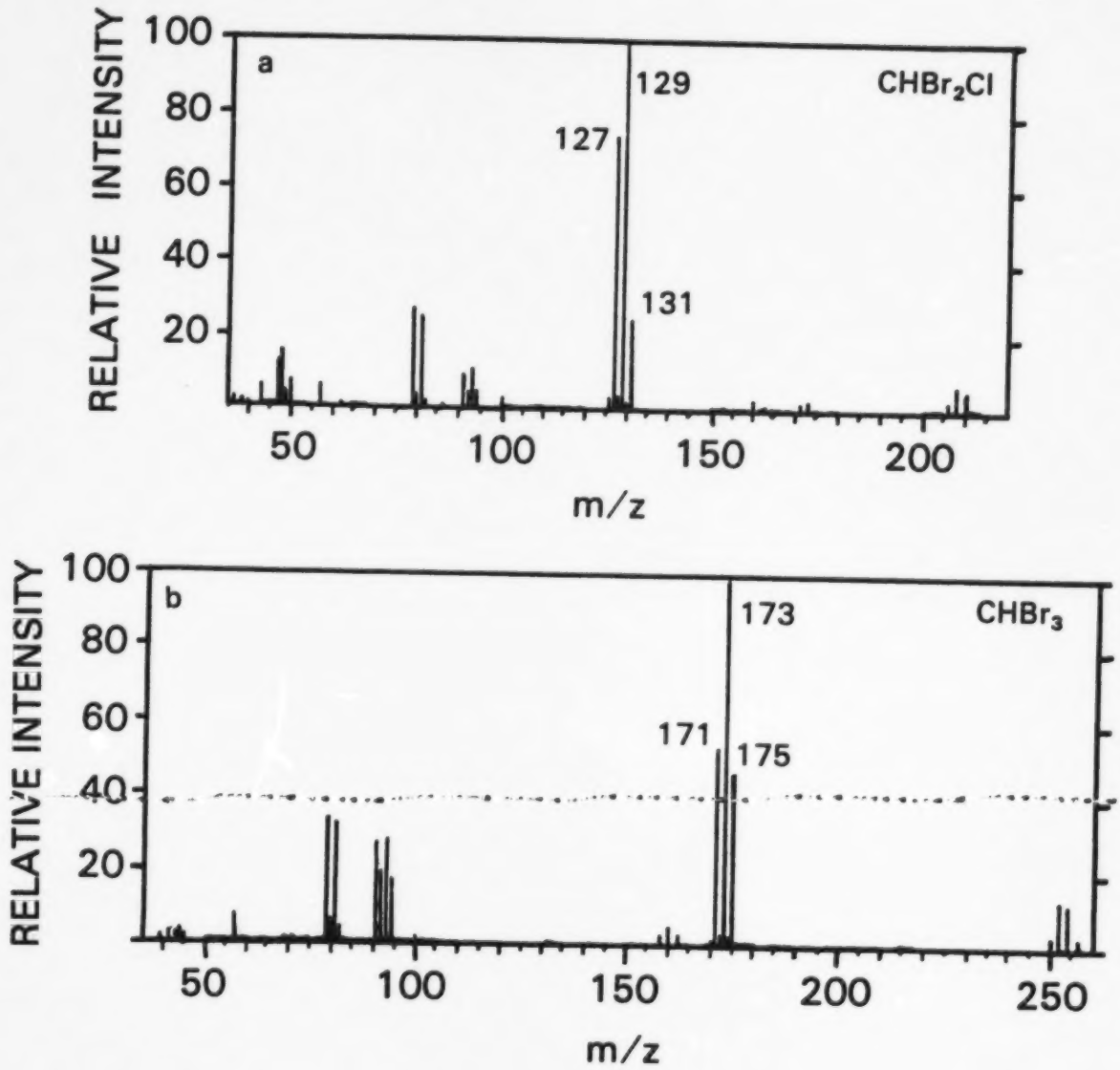

Figure 4. Mass Spectra Of Chlorodibromomethane (a) And Bromoform (b)

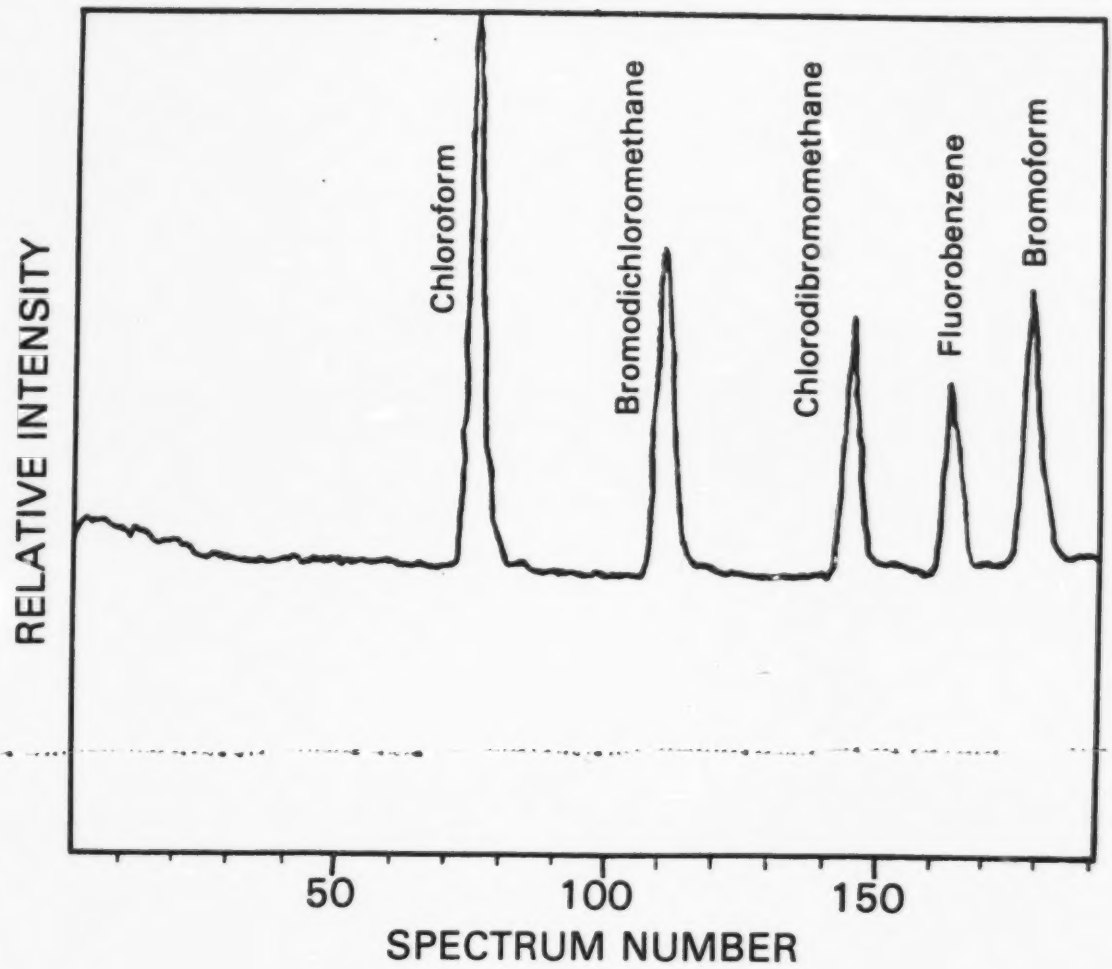

Figure 5. Selected Ion Current Profile Of Trihalomethanes And Internal Standard/Surrogate Compound

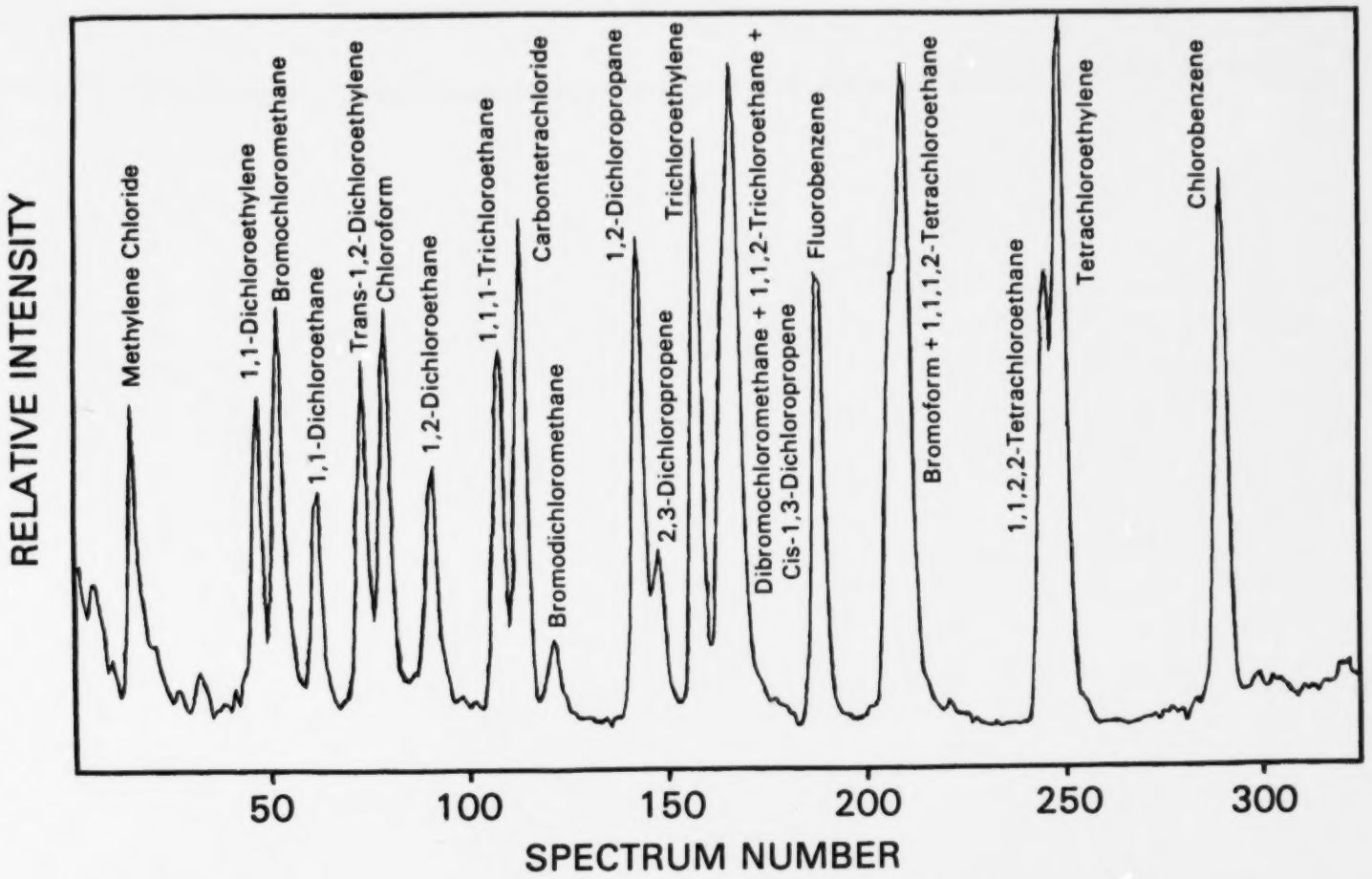

Figure 6. A Total Ion Current Profile Of Organohalides